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This letter covers the reporting period of the subject contract from May 15 to August 15, 1965. Major activities of the principal investigators during this period were as follows:

I WORK IN PROGRESS

- (1.1) Martian Atmospheric Compositional Analysis: Its Biological Significance - Considerable attention was devoted during the reporting period to problems of ascertaining the potential biological significance of what have heretofore been termed "environmental" measurements. Major effort has been devoted to a joint study with J. E. Lovelock of the potential biological significance of atmospheric compositional analysis. A paper reporting the results of this study is in preparation; a preliminary draft of this paper is included in this report.
- (1.2) Order Recognition Studies - During the reporting period, detailed studies were initiated to define and construct measures of order in arrays of physico-chemical and other data. This project, being carried on in cooperation with J. E. Lovelock, will provide the basis for a computer-implemented simulation study as an initial test of the utility of the proposed measures. A preliminary report of this work is being drafted.
- (1.3) Voyager Payload Compatibility Review - At the request of the Office of Bio-Sciences Programs, contract personnel performed a review of the scientific compatibility of a number of proposed Voyager payloads and presented the results of the review in an informal report.

II FIELD TRIPS

- (2.1) J. E. Lovelock - A visit was made to the laboratory of J. E. Lovelock at Bowerchalke, England, for the following two purposes:
  - (2.1.1) Detailed discussion of the proposed paper on Martian Atmospheric Compositional Analysis alluded to in paragraph (1.1) above.
  - (2.1.2) Preliminary analysis of the problem of order recognition in biology (paragraph 1.2 above).
- (2.2) Jet Propulsion Laboratory - In connection with paragraph (1.3) above, the principal investigators visited the Jet Propulsion Laboratory to obtain supplementary information about certain of the experiments and instrumentation proposed for Voyager.
- (2.3) Bell Telephone Laboratories - Two visits were made to the Bell Telephone Laboratories at Murray Hill, New Jersey, to obtain a digital spectral analysis program for use in the order recognition project.

Dian R. Hitchcock  
Dian R. Hitchcock

Gordon B. Thomas  
Gordon B. Thomas

MARTIAN ATMOSPHERIC COMPOSITIONAL ANALYSIS: ITS BIOLOGICAL SIGNIFICANCE

D. Hitchcock and J. E. Lovelock

The purpose of the inquiry reported here is to explore critically and in more detail the thesis presented recently by one of the authors [J.E.L.(1)] that physical and chemical characteristics of a planetary environment can provide direct evidence of a biota.

There is wide agreement among space scientists whose primary orientation is the physical sciences, that experiments to observe physical properties of the surface and atmosphere of Mars should be given a high priority. What is not so widely understood is that many of the same kinds of physical measurements are also capable, in principle, of providing much information of great utility to biologists whose primary concern is determining whether or not life forms have evolved on Mars, and, if so, what such life forms are like.

It has been frequently pointed out that, in order to understand the kind of life that may exist on Mars, it is necessary to obtain information regarding those properties of the atmosphere and surface to which any evolving Martian life form must have adapted. What is less frequently observed is that information regarding these "environmental" features of Mars may constitute direct and primary evidence of life in the form of observed effects which cannot be accounted for by postulated abiological processes.

This conclusion--that observations of purely physical properties may provide data which support the conclusion that life exists on Mars--follows directly from one fundamental and highly plausible assumption (1). This is the assumption that the entropy of living systems is low relative to their non-living environments. Two consequences of this assumption are relevant to the present inquiry. The first is that living systems, which are continuously reacting with their environments, will drive those environments to a state of physical or chemical disequilibrium which will be recognizable as such if available observations of the state of that environment are sufficiently complete to rule out explanations which account for those observations in terms of solely abiological processes. The second consequence is that there will always exist an entropy gradient between living systems and their inorganic environments; furthermore, the origin of non-living biogenic material will be revealed by the existence of such a gradient for a period of time which will vary depending on the rate of attainment of equilibrium as determined by local conditions, but which can be expected to be measurable in units of at least  $10^5$  years, and thus is exceedingly long compared to the lifetimes of the organisms themselves.

Given that the presence of life is characterized by a state of physical and chemical disequilibrium of the system consisting of life-plus-its-local-environment, the next question is whether or not essential disequilibria can be effectively diagnosed from practical observations. If life exists on Mars, then the atmosphere of Mars is probably an important part of its chemical environment. Consequently, we might suppose that the composition of an atmosphere should reflect the presence of life forms on Mars, on the plausible assumption that such life forms continuously react either directly or indirectly with it. The objective of the inquiry reported here is to review critically the potential biological significance of two types of atmospheric data. The first kind of data is that regarding the relationship between the atmosphere and surface material, as revealed by an experiment designed to detect a free energy gradient between the two.\* The second

\* The experiment was developed by J.E. Lovelock and his colleagues at the University of Houston.

consists of observations of the concentrations of selected major and trace components of the atmosphere including isotopic abundances. Although these two experiments differ greatly in terms of their implementation, interpretability, and potential biological significance, they are here classed together because both represent ways of implementing a strategy of life detection based on a search for evidence of disequilibria and because common to both is the assumption that the atmosphere is a relatively homogeneous medium which reflects processes occurring over the whole surface of the planet.

#### LIFE DETECTION BY MEANS OF DETECTION OF CHEMICAL FREE ENERGY IN SURFACE MATTER

It has been pointed out above that one of the consequences of the assumption that the entropy of living systems is low relative to their non-living environments is that there will always exist an entropy gradient between the two. After death, the free energy stored up in a living system is gradually dissipated into the surrounding local environment until, eventually, the matter which once comprised the living system is no longer characterizable as a region of relatively low entropy.

The most likely site for life on a planet is the surface-atmosphere interface. Here the solid surface and the gas and liquid phases meet at the point of maximum absorption of the solar energy flux and maximum temperature, so that a diversity of raw material--providing both by the relatively mobile atmosphere and the less readily transported surface matter--are available simultaneously with the energy necessary for their biotic transformation.

The synthesis of biotic compounds from simple abiotic molecules requires the dissociation of the latter and the incorporation of some of the reactive dissociation products in large complex molecules. The lysis of simple inorganic molecules, such as water and carbon dioxide, not only releases reactive products to be used in the synthesis of biological molecules, but also releases simple active molecules like oxygen into the atmosphere. This incorporation of reactive dissociation products into complex living molecules and the release of simple active molecules therefore results in the storage of chemical free energy in these biotic molecules. If they are large--and they are--they are relatively non volatile and, hence, tend to accumulate at the surface atmosphere interface. Life, therefore, tends to generate a metastable condition between the surface and the atmosphere with a sharp chemical free energy boundary at the interface.

Perhaps the simplest experiment in life detection, therefore, is to look for a chemical free energy difference between Martian surface matter and the atmosphere. One very promising such experiment consists of heating two aliquots of a sample of surface material, one in an inert gas such as argon or nitrogen, and the other in the Martian atmosphere. The temperature of each sample is recorded. A combustion reaction between the sample and its own atmosphere produces an excess of heat, whereas heat changes due to inorganic transitions will be equal in both samples. Thus, the occurrence of such a combustion is detected as a difference in temperature between the sample heated in the atmosphere and that heated in the inert gas. The combustion of surface organic matter from a planet with an oxidizing atmosphere takes place with a considerable liberation of heat. If the planet has a reducing atmosphere, a lesser but still observable heat production could be expected to follow the reduction of the more oxidizable metastable biotic molecules. If the constituents of the atmosphere are known, additional information can be obtained from noting the temperature at which the combustion occurs, and from examining the volatile pyrolysis products. It is debatable whether such an experiment is subject to false positives of any sort except, of course, those resulting from machine errors or inadvertent contamination of the equipment prior to launch. For example, sulfide rocks will burn on heating in air (but their ignition temperature is different from that of organic matter). On Earth, however, at least some sulfide rocks are thought to be of biological origin. It would seem that if the fundamental assumptions on which this experiment are based--those central to the definition of life in terms of its entropy-reducing function--are valid, then evidence

of chemical free energy gradients between surface matter and the atmosphere should always be construed as prima facie evidence of life.

### MARTIAN ATMOSPHERIC COMPOSITIONAL ANALYSIS

Experiments designed to identify and determine the relative quantities of major and trace components making up the Martian atmosphere may be recommended on many grounds. The utility of such measurements to scientific programs which are not primarily concerned with Martian biology need not be stressed here. Similarly, the value of such data to engineers is enormous, and it can also be said to constitute almost a prerequisite to satisfactory interpretation of the results of analyses of organic content to surface material, culture experiments and other experiments designed to demonstrate the existence of Martian life forms through direct observation of such forms. The assumption that the atmosphere of Mars, like that of Earth, is relatively homogeneous in that its composition does not vary greatly with location on the surface of the planet and its reflects processes occurring over the whole surface, implies that such an experiment is not likely to be site limited. (The probability that such an experiment will be performed near an active volcano and hence record results which cannot be extrapolated to other locations is negligible; furthermore, the availability of corroborative data makes it possible to distinguish such a situation, so that there is a high probability that even these kind of data could be usefully and appropriately interpreted.) For these reasons, one or more forms of atmospheric analysis experiments deserve and receive a high priority. The primary disadvantage that may at this time be urged against such experiments as part of a biological exploration program is that they apparently do not have a potential for providing direct or relatively conclusive evidence of life on Mars.

It was pointed out above that one might on very plausible theoretical grounds suppose that life forms on the planet in continuous interaction with the atmosphere would drive that segment of the environment to a state of chemical or physical disequilibrium which will be recognizable as such if available observations of its state are sufficiently complete. The purpose of this inquiry is to review critically the claim that an analysis of the atmosphere of Mars can provide data which can be interpreted as indicative of the presence of life forms. A Martian atmospheric analysis cannot be advocated as a good life detection experiment if terrestrial atmospheric data does not provide good evidence for the existence of terrestrial life. If, however, a good case can be made for the position that the presence of terrestrial life can be demonstrated from evidence consisting wholly or largely of observed concentrations of atmospheric constituents, then a Martian atmospheric analysis ought to receive very high priority as an exobiological experiment, and care should be exercised to insure that atmospheric experiments conducted are designed so as to provide the greatest amount of potentially significant biological data.

For these reasons, the method followed in the first stages of this inquiry has been to treat the employment of terrestrial atmospheric data as evidence for terrestrial life and an analogue of the Martian case, and to attempt to answer the following questions:

1. Does the terrestrial atmosphere reflect the presence of life on Earth?
2. Can the presence of terrestrial life be inferred wholly or largely from observations of the major and/or trace components of the terrestrial atmosphere?
3. What additional data regarding purely physical properties of the planet are necessary to such an interpretation?

TABLE I

#### Chemically Active Components of the Atmosphere

| <u>Gas</u>      | <u>Ratio by Volume</u> | <u>Remarks</u>       |
|-----------------|------------------------|----------------------|
| N <sub>2</sub>  | 0.78                   | Mixed in troposphere |
| O <sub>2</sub>  | 0.21                   | Mixed in troposphere |
| CO <sub>2</sub> | 3 x 10 <sup>-3</sup>   | Mixed in troposphere |

| <u>Gas</u>         | <u>Ratio by Volume</u>                        | <u>Remarks</u>               |
|--------------------|---|------------------------------|
| H <sub>2</sub> O   | 10 <sup>-5</sup> to 10 <sup>-2</sup>          | Dissociates in mesosphere    |
| O <sub>3</sub>     | 10 <sup>-7</sup> to 10 <sup>-8</sup>          | Peak in stratosphere         |
| CH <sub>4</sub>    | 1.5 x 10 <sup>-6</sup>                        | Dissociates in stratosphere  |
| N <sub>2</sub> O   | 2.5 x 10 <sup>-7</sup>                        | Dissociates in stratosphere  |
| H <sub>2</sub>     | 5 x 10 <sup>-7</sup>                          | Dissociates in thermosphere  |
| CO                 | 5 x 10 <sup>-8</sup>                          | Variable, industrial as well |
| NO·NO <sub>2</sub> | 5 x 10 <sup>-10</sup> to 2 x 10 <sup>-8</sup> | as atmospheric origin        |

Table I from the data quoted by Nicolet (2) shows the composition of the Earth's atmosphere. A cursory examination of this table reveals the simultaneous presence of gases which are either chemically incompatible with one another or whose continued existence is incompatible with known physical conditions of temperature, radiation flux, etc. If we assume that the concentrations of the atmospheric constituents do not change with time, then the observed concentrations of incompatibles must be accounted for in terms of a steady state rather than a simple thermodynamic equilibrium. This implies that we must account for the presence of these gases in terms of reactions which remove them from the atmosphere and others which, by replacing them, maintain the observed concentrations. These removal and replacement processes may be divided into two classes:

1. Those which are "physical" abiological processes which, like the ozone producing action of the solar flux, can be expected to occur in the absence of a biota.
2. Those which are either directly attributable to the action of a biota, or are inconsistent with the hypothesis that the atmosphere is the result of solely abiological processes.

An examination of Table I also reveals the simultaneous presence of a number of gases which are compatible in that their long term continued presence in some concentrations is not inconsistent with known physical conditions. The concentrations observed may be due solely to abiological processes, or may be partly affected by biological mechanisms, and in the latter case the presence of a biota may be reflected in the occurrence of anomalously high or low concentrations of such gases.

It would thus appear that atmospheric evidence of a biota would, if present, occur in the form of observations of one or more incompatibles for whose presence no satisfactory abiological mechanism can be postulated, and/or in the form of anomalously high or low concentrations of gases whose presence at some concentration is otherwise to be anticipated on abiological grounds.

Among the constituents whose relative concentrations seem indicative of a terrestrial biota are oxygen, methane, and carbon monoxide. In addition, the concentrations of carbon dioxide, hydrogen and the oxides of nitrogen may be anomalous and worth closer examination. The arguments supporting the position that these constituents have biological import are outlined below.

### Oxygen and Methane

The fact that 20 per cent of the Earth's atmosphere is oxygen is not, in itself, conclusive evidence that life exists here, although many, in attempting to account for the oxygenic concentration, have argued an important biological role from the known photosynthetic production of oxygen. These arguments may be countered by the observation that biotic consumption of respiratory O<sub>2</sub> may account for all that is photosynthetically liberated, so that the total available quantity is not influenced by the biota.

The origins of the terrestrial atmosphere are not well understood, and indeed are of only slight relevance to the subject presented here.

That the terrestrial atmosphere was at one time a reducing atmosphere seems well established. The nature of the exact mechanisms responsible for the loss of hydrogen and the consequent transformation to an oxidizing atmosphere are uncertain. That photolytic decomposition of  $H_2O$  played a significant role in this transformation is unquestionable, although there is disagreement as to its extent. What is important to note is not the disagreement, but the fact that this is the only abiological mechanism offered to account for the loss of hydrogen and the release of  $O_2$ . This process is still going on, though at a lower rate than during the early history of the Earth, due to the fact that the high concentration of  $O_2$  limits the efficiency of the photolytic process (3). The present estimate based on known current loss of  $2.5 \times 10^7$  atoms of hydrogen  $cm^{-2}sec^{-1}$  corresponds to a total  $O_2$  production of approximately  $6 \times 10^6$  molecules  $cm^{-2}sec^{-1}$ .

A review of the concentrations of trace components in the atmosphere reveals that methane is present to the extent of 1.5 parts per million. The presence of methane is chemically incompatible with that of oxygen on a long-term basis, since oxygen reacts with the latter to form oxides of carbon and hydrogen. Hence the presence of methane implies a consumption of oxygen and a replacement of the oxidized methane. The rate of oxidation of methane is very low in the lower atmosphere, but exceedingly rapid in the upper atmosphere. At 70 km the half life of methane is about three hours (4). The rate of oxidation, consequently, is dependent on the speed of transport to regions where methane is more rapidly oxidized, which is accomplished by mixing and diffusion, of which the latter is the slower mechanism. Nicolet (2) estimates from atmospheric data that the diffusion flow of methane into the region of 100 km is  $7 \times 10^6$  molecules  $cm^{-2}sec^{-1}$ , which may be taken as corresponding to the minimum oxidation rate. If we assume that oxidation of one molecule of methane consumes at least three molecules of oxygen giving rise to  $CO + 2H_2O$ , then it follows that the consumption of oxygen by this process is  $2.1 \times 10^7$  molecules  $cm^{-2}sec^{-1}$ , which is more than three times the estimated rate of production of  $O_2$  from photolytic decomposition. It will be noted that the estimates of  $O_2$  production assume that all hydrogen lost from the atmosphere is the consequence of decomposition of  $H_2O$ ; however, it should be borne in mind that if there are other mechanisms resulting in the production of molecular hydrogen, without the consequent production of  $O_2$ , the estimates of the abiological production of  $O_2$  may be excessive. These considerations lead to the conclusion that there are additional sources of  $O_2$  than photolytic decomposition of  $H_2O$ ; that these sources are in all likelihood biological in nature would seem to follow from the failure of aeronomists to postulate alternative abiological  $O_2$  production mechanisms to account for the transition from reducing to oxidizing conditions.

These arguments are based only on the observed concentrations of  $O_2$  and methane, the rates of the postulated photolytic  $O_2$  production and an assumed diffusion flow and oxidation of methane.

The inferred rate of methane oxidation is probably very conservative, since it requires a methane replacement which is less than  $7 \times 10^6$  molecules  $cm^{-2}sec^{-1}$ . Annual production of methane from biological sources (enteric fermentation by large ungulates and marsh gas) is estimated at 1 to  $2 \times 10^{10}$  molecules  $cm^{-2}sec^{-1}$  (5) which requires for its oxidation more than 2,000 times as much oxygen as is annually produced by photolytic decomposition.

The minimum methane oxidation rate considered above is based on minimum estimated rates of diffusion into regions of 100 km or more. In fact, methane is oxidized at low altitudes, and more realistic oxidation rates could be calculated from the observed concentrations although we have not made such calculations. It is instructive to note, however, that such a "realistic" methane oxidation rate which implies a methane half-life as long as 100 years corresponds to  $10^{10}$  molecules  $cm^{-2}sec^{-1}$  and requires at least three times that many O atoms (on the assumption that the reaction produces  $CO + 2H_2O$ ).

It should be observed that oxidation of biologically produced methane does not support the conclusion that the terrestrial biota is responsible for a total net production of excess  $O_2$ . In fact, it provides no more support for the conclusion that the biota is responsible for the past oxygenic concentration of the Earth's atmosphere than does the observation that  $O_2$  is photosynthetically liberated. The point is that we are not here concerned with the origin of the atmosphere, but only with the present atmosphere as evidence of a present biota. Methane and oxygen are chemically incompatible on a long-term basis, and the presence of these two gases in their observed concentrations permits one to infer that photolytic decomposition cannot be the only source of  $O_2$ , and this, in turn, requires that we look for some other source. It is failure to envisage an acceptable abiological alternate production mechanism which supports the inference of a biota. The argument would be equally well supported if some other incompatible gas of unknown origin occurred instead of the methane.

The above discussions have focused on the simultaneous presence of  $O_2$  and methane as providing evidence that the maintenance of the observed oxygen concentration requires a biological explanation. The inferred methane oxidation rate also requires an explanation in terms of a methane replacement mechanism. The formation of methane in an oxidizing atmosphere from the simpler available components  $H_2O$  and  $CO_2$  is chemically almost impossible because it is not a simple reaction, but a sequential one involving highly unlikely steps requiring the persistence of highly reactive intermediate compounds. Methane can, of course, be produced in a reducing atmosphere at high temperatures, and there now seems little doubt that methane was at one time a major constituent of the early terrestrial reducing atmosphere. This methane could not have persisted in the atmosphere during its transformation to an oxidizing atmosphere. That it could have remained sequestered from the atmosphere during the long period since oxygen became a primary constituent, now to appear as an outgassed product is not a tenable hypothesis. Methane would not survive the temperature, pressure and chemical conditions deep in the Earth. This does not necessarily apply to Mars, where, so far as we know, temperature and pressure conditions within the planet may not be comparable. It will be noted, of course, that if the atmosphere of Mars is a reducing one, then the observation of methane as a constituent of it cannot necessarily be invoked in support of the hypothesis of its biological genesis, unless it is known that the UV flux on Mars is sufficient for its rapid removal and the prevailing surface conditions preclude its abiological replacement.

#### Carbon Monoxide and Carbon Dioxide

The concentration of CO in the atmosphere varies from .05 to 2 parts per million at the surface, the higher figures encountered in areas of concentrated industrial activity. We may, therefore, take the lower figure as more representative of the total terrestrial atmosphere. The significance of this constituent derives from the fact that its concentration is suspiciously low when considered in conjunction with abiological mechanisms capable of removing it from the atmosphere, and with the postulated rates of its formation as a by-product of methane oxidation.

Carbon monoxide is extremely stable in the terrestrial atmosphere. Massey (4), in considering the significance of the low CO concentration, considers three possible oxidation processes, all of which are very slow.

Massey does not estimate the half life which could be expected if CO were oxidized only by these means. However, some idea of the extreme slowness of these reactions can be obtained from the observation that they do not seem to be able to account for the transformation of  $C^{14}O$  into  $C^{14}O_2$ . Thus, both Massey and others (6) have observed that a more rapid CO oxidation mechanism must be invoked, in order to account for the widespread abundance of  $C^{14}O_2$  and the introduction of  $C^{14}$  into the photosynthetic cycle, since the primary product of neutron bombardment of air is carbon monoxide rather than carbon dioxide. It may, therefore, be speculated that a CO half life not less than about 1,000 years and more probably as much as 8,000 years, is to be expected if these abiological oxidation processes were the sole existent ones.

On the assumption that the available abiological CO oxidation processes give rise to a CO half life not less than 100 years, we may now inquire whether the known relative abundances of atmospheric constituents are consistent with such slow processes, or whether they require the assumption of a more rapid biological CO oxidative mechanism to explain them.

In the discussion of the significance of O<sub>2</sub> and methane, we suggested that atmospheric data support the hypothesis that methane is oxidized at a rate not less than  $7 \times 10^6 \text{ cm}^{-2}\text{sec}^{-1}$  (based on diffusion into upper atmosphere) and more probably on the order of to  $10^{10} \text{ cm}^{-2}\text{sec}^{-1}$  (corresponding to a hypothetical "realistic" rate which considers oxidation reactions at other altitudes). For the purpose of that discussion, which considered minimum O<sub>2</sub> consumption consistent with the observed methane concentration, it was assumed that methane was oxidized to CO and H<sub>2</sub>O since such a reaction requires less oxygen than would be the case if CO<sub>2</sub> were formed. The exact proportion of CO among the reaction products of the low temperature oxidation of methane in the atmosphere is unknown, but it seems clear that the proportion is significant. Thus methane oxidation is a process which produces atmospheric CO, and rough estimates of the amounts contributed from this source may be made on the basis of assumed oxidation rates and CO yields.

If we assume that 50 per cent of the carbon is oxidized to carbon monoxide, then the hypothesized "realistic" oxidation rate of methane corresponds to an annual production of  $3.4 \times 10^{13}$  grams of CO. This estimated annual production of CO may be combined with the known atmospheric concentration of .05 parts per million to arrive at an estimate of 4.6 years as the carbon monoxide half life consistent with the latter concentration; even if the concentration were 0.2 parts per million, the half life would be 18.2 years. It is clear then that, unless carbon monoxide oxidation is effected by the abiological processes proposed at much greater rates than seems to be the case, these cannot be the only oxidation processes available. The extent of the discrepancy is more clearly illustrated by the fact that a concentration of ten parts per million would be expected from this rate of CO production if the half life were in fact 1,000 years. Even quite small assumed methane oxidation rates and CO yields are inconsistent with the observed concentrations; for example, an annual production of  $1.7 \times 10^{13}$  grams implies a half life of 10.2 years or a concentration of five parts per million.

The actual production of CO would appear to be much greater than the estimates presented above. The known annual production of methane from biological sources is 4.5 to  $9.0 \times 10^{13}$  grams (5). Taking the mean of these figures as the annual production and assuming a 50 per cent CO yield we arrive at a total of  $5.6 \times 10^{13}$  grams from this source alone. To this must be added the CO produced from combustion of fossil fuels and forest fires.

According to Haagen-Smit (7) 40 per cent of the weight of gasoline consumed in internal combustion engines emerges as CO. This corresponds to a world-wide annual production of CO from internal combustion engines alone of  $3 \times 10^{14}$  grams. CO is also produced by other fossil fuel combustion and by prairie and forest fires. We do not know the actual CO yield from these sources, but the total of fossil fuel carbon oxidized annually is  $3 \times 10^{15}$  grams, whereas forest and prairie fires represent the oxidation of  $1.6 \times 10^{15}$  grams.\* If we make the assumption that the ratio of carbon oxidized to CO to that oxidized to CO<sub>2</sub> is one to 1,000, then the annual yield from these two sources is  $1.1 \times 10^{13}$  grams. The resulting total, including methane, gasoline, other fossil fuel consumption and forest and prairie fires, is  $3.7 \times 10^{14}$  grams of CO per year. If these figures are correct, then they imply a half life of CO of less than 0.4 years in order to maintain the current concentration of 0.05 parts per million; in contrast, if the removal mechanisms now available result in a 1,000-year half life, the concentration should be about 100 parts per million. It seems to

\*These calculations are based on data taken from Hutchinson (5) and Schurr (8).

us that the conclusions that a far more rapid removal mechanism is operating is inescapable. That is, a biological mechanism would seem to follow from the inability to postulate an acceptable oxidation mechanism to explain the rapid conversion of  $C^{14}O$  to  $C^{14}O_2$ .

The latter conclusion is further buttressed by a consideration of the known capacity of the biota to fix atmospheric carbon monoxide.

It should also be observed that  $NO$  is also readily fixed biologically, and, like  $CO$  is produced in large quantities from fossil fuel combustion. It is also produced in the upper atmosphere in substantial amounts. It may be that the same arguments regarding the low concentration of  $CO$  also apply to  $NO$ , which is present to the extent of  $10^{-9}$ , and that this concentration can also be construed as partial evidence of the existence of a terrestrial biota.

We can at this time propose no good arguments in support of the position that the observed concentration of  $CO_2$  is inconsistent with the hypothesis that its concentration is governed largely by abiological processes.  $CO_2$  is a known constituent of volcanic effluents (although it may be questioned whether the  $CO_2$  currently produced by volcanoes is not fossil  $CO_2$  originally laid down in limestone deposits as the result of biological activity). We may, however, assume that large amounts of juvenile  $CO_2$  (that is, not of fossil origin) were introduced into the secondary atmosphere. Urey (9) has proposed that the amount of  $CO_2$  present before life arose was determined by the reaction of surface magnesium and calcium carbonate (in the presence of  $H_2O$ ). Hutchinson (5) while agreeing with Urey that this reaction might serve to hold the atmospheric concentration to a level not much greater than the present, points out that at  $25^\circ C$  the pressure of  $CO_2$  in equilibrium with magnesium carbonate and silicate is  $10^{-5}$  atm., or about one thirtieth of the observed  $CO_2$  pressure in the atmosphere. He holds, however, that the general mobility of the Earth's crust and the existence and structure of the biosphere will give rise to a pattern of distribution which will never approach equilibrium at all closely. On this view, it could be anticipated that a more careful re-examination of the possible abiological processes which produce and remove  $CO_2$  would reveal that these processes do not account for the observed levels.

Even though few biological inferences can be drawn from the observed concentration of  $CO_2$  in the atmosphere, the presence of  $C^{14}O_2$  is of considerable importance, if preceding arguments supporting the hypothesis of a biological  $C^{14}O$  to  $C^{14}O_2$  oxidation mechanism are valid. The ratio of these compounds in the products of neutron bombardment of air at one atmosphere is approximately 88:12 (6). It is clear that under abiological conditions characterized by a  $CO$  oxidation rate that is very slow relative to the half life of  $C^{14}$  one would expect to find the specific activity of  $CO$  high relative to that of  $CO_2$  if the relative concentrations of these two compounds were close to their present values. Under these conditions the differences in specific activity of these two compounds is proportional to the difference in the size of their pools (including not only that circulating in the atmosphere, but also all that reversibly adsorbed at the surface of the earth) and the ratio of their occurrence in the products of neutron bombardment. Thus, the smaller the ratio of  $CO$  to  $CO_2$ , the greater the relative specific activity of the former should be; similarly, the greater the proportion of  $CO$  in the bombardment products, the greater its activity.

The capacity of the biota to transfer carbon compounds rapidly between pools implies that under preindustrial conditions the specific activities of the two did not show a great disparity and were probably about equal. Under present industrial conditions characterized by the release of large quantities of inactive  $CO$ , the ratio of  $C^{14}O$  to  $C^{14}O_2$  would tend to be even further depressed. This is a transient condition and equilibrium would again be established given a constant rate of  $CO$  production. It is clear that measurements of the relative concentrations and activities of  $CO$  and  $CO_2$  are potentially of great biological significance, although the arguments presented

here should be more carefully examined. They are included because this line of reasoning suggests that the CO activity might be very high indeed under abiological conditions and, therefore, easy to measure.

### Other Constituents

There are other minor constituents of the atmosphere whose concentrations are undoubtedly affected by the presence of the biota, in particular, nitrous oxide and hydrogen. Both of these compounds are known to be produced biologically in significant quantities. Postulated abiological production mechanisms\* could produce these gases at rates comparable to their biological formation. In these circumstances their observed concentrations do not provide an adequate index to the nature of their origin. When more is known about the possible abiological sources of these constituents, and firm figures can be attached to the resulting anticipated concentrations, their validity as biological indicators can be determined. They are mentioned here because their occurrence in other concentrations on other planets may have a more obvious biological significance.

The value of knowledge of concentrations of stable isotopes in the atmosphere is of such well established biological significance that it need not be stressed here.

Let us now turn to a consideration of the possible biological significance of a Martian atmospheric analysis. The objective of this inquiry into the biological significance of the terrestrial atmosphere was to determine whether an atmospheric analysis could appropriately be viewed as a life detection experiment. The following conclusions would seem to follow from the preceding discussion:

1. Not only is the presence of a terrestrial biota reflected in the atmosphere, but it can be inferred largely from atmospheric data alone; in particular, no assumptions regarding the detailed nature and biochemistry of the biota are necessary to such an interpretation.
2. The biological significance of an atmospheric mixture lies in the relative concentrations of a variety of constituents, and does not reside wholly in the presence or absence of any single one of them. Such a mixture is biologically significant if it represents a departure from a predictable inorganic steady state; the strongest evidence comes from the observation of the simultaneous presence of two gases, like methane and oxygen, capable of undergoing irreversible reactions; even with gases whose presence can be expected under abiological conditions, departures from the abundances to be anticipated will be of biological import.
3. It is clear that the presence of even very minor constituents may be very significant; consequently, every attempt should be made to provide as complete an analysis of the atmosphere as possible.

### MARTIAN BIOLOGICAL ATMOSPHERIC EXPERIMENT

By analogy with Earth, Martian life, if it is present, may affect Mars' atmosphere by giving rise to anomolous concentrations of compounds whose presence could be expected as a consequence of purely inorganic reactions and/or by concentrating in the atmosphere certain compounds which, like methane, are incompatible on a long-term basis with other constituents

It might be argued that life detection by means of atmospheric analysis is more appropriate for planets which, like the Earth, have a high density of living matter at or near the surface, but inapplicable to planets on which the biota, if present, is likely to be very thin. In this connection it should be pointed out that the ratio

\*See, for example, Cadel (10)

of surface area to atmospheric mass is 30 times less for Mars than for the Earth, so that the quantity of living matter required to produce comparable effects could be much less. Furthermore, it is conceivable that the removal of one component biologically produced is dependent upon the simultaneous presence of another similarly produced. If the removal rate is concentration dependent, it is possible for an easily measured steady state concentration to occur even when the production rate is very low. A more fundamental point is that the ability of a biota to control its environment and drive it to a state of low entropy is not a function of the density of that biota, but rather follows from the tendency of life to continue growing and developing until the supply of available raw materials establishes a limit. Consequently, the detectability of a planetary biota by means of atmospheric compositional analysis is not necessarily limited by the density of that biota.

On Mars a life detection experiment based on atmospheric compositional analysis should be designed to measure the abundances of as many of the components of the atmosphere as is possible, including not only the important major components but also the trace components. In view of what is not known of the Martian atmosphere or surface, it is unwise at this stage to prejudice the experiment by guesses at what may be the more significant constituents to measure. The detailed significance of any single compound can be determined only after the compositional data have been obtained and interpreted. Such interpretation clearly requires at least a minimum of supporting data so as to make possible the specification of the conditions under which these components would be expected to react. Some of these auxiliary data such as the solar spectrum and the temperature at the surface are already available; others, such as the state of oxidation of the surface and the radiation flux at the surface may be made available during the course of the early Voyager missions. It should be pointed out that these latter data may not be necessary to the unequivocal interpretation of the biological significance of the atmospheric data; that these would have value in confirming any conclusions is clear. If, as is possible, the Martian atmosphere is poised between an oxidizing and a reducing state, knowledge of the oxidation state of the surface would clearly be of great value.

Information regarding isotopic concentrations may also be of considerable importance. In particular, where the same element occurs in two or more atmospheric compounds, a comparison of its isotopic abundances in the different compounds provides valuable information on the nature of the reactions amongst them. The well known ability of living organisms to fractionate isotopes of the same elements provides a means of distinguishing biotic and abiotic reactions; thus, evidence of clear isotopic selectivity would be very suggestive evidence of biotic transformation.

Although any measures of isotopic abundances would appear to have definite value, the measurement of  $C^{14}$  activity in atmospheric  $CO_2$  and, if possible, that of  $CO$  would seem to be of unusual interest. In view of the likely small pool sizes of each of these components on Mars, the specific activity of each is likely to be much higher than on Earth. We do not at present know the yield of  $C^{14}O$  relative to  $C^{14}O_2$  to be expected from neutron bombardment of the Martian atmosphere, but in the absence of atmospheric oxygen, it might be expected that the  $CO:CO_2$  ratio is even higher than on Earth. If, as seems likely, the arguments regarding the slowness of  $CO$  oxidation apply equally well to Mars, then one would expect very great disparity in the  $C^{14}$  activity of the two compounds. Failure to find it would suggest a rapid biological  $C^{14}O$  fixation.

Even if the  $CO$  activity cannot be measured, a measurement of the  $C^{14}O_2$  activity alone might be highly significant, since the amount to be expected under abiological conditions is clearly a function of  $CO$  oxidation rate, pool size, and  $C^{14}O:C^{14}O_2$  yield from neutron bombardment.

Other isotopic measurements which deserve mention are  $D$  and  $H$  abundances in water and hydrogen or other hydrides, and the ratio of  $N^{14}$  to  $N^{15}$  in nitrogen oxides.

## REFERENCES

- (1) Lovelock, J. E., A Physical Basis for Life Detection Experiments, Nature, in press.
- (2) Nicolet, M., Reactions and Photochemistry of Atoms and Molecules, Disc. Farad. Soc. 37, 7 (1964).
- (3) Urey, H. C., Primitive Planetary Atmospheres and the Origin of Life, Symp. Int. Union. Biochem., Moscow, 1957 (The Macmillan Company, New York) I, 16 (1959).
- (4) Massey, H. and Potter, A. E., Atmospheric Photochemistry, Lecture Series 1961, Number 1, The Royal Institute of Chemistry.
- (5) Hutchinson, G. E., Biochemistry of the Terrestrial Atmosphere, Chapter 8 in Kuiper (ed.), The Solar System, vol. II, The Earth as a Planet, (The University of Chicago Press, Chicago) (1954).
- (6) MacKay, C., and Wolfgang, R., Free Carbon Atom Chemistry, Science 148, 899 (1965).
- (7) Haagen-Smit, A. J., The Control of Air Pollution, Sci. Amer., 210, 24 (1964).
- (8) Schurr, S. H., Energy, Scientific American, 209, 110 (1963).
- (9) Urey, H. C., The Planets: Their Origin and Development, (Yale University Press, New Haven), (1952).
- (10) Cadle, R. D., Daytime Atmospheric O (<sup>1</sup>D), Disc. Farad. Soc., 37, 66 (1964).